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Solvent-free conversion of CO$_2$ in carbonates through a sustainable macroporous catalyst

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The novelty of this work consists of synthesizing and exploiting a heterogeneous catalyst containing ammonium chloride as part of the polymeric sponge sites for CO$_2$ capture. To this aim, the polymerization of 2-acryloyl(oxyethyl)trimethylammonium chloride was performed in cryo-condition, in the presence of a crosslinking agent, obtaining a lightweight macroporous freestanding material. Its efficiency in converting aromatic and aliphatic epoxides to the corresponding carbonates was successfully proved by using proton Nuclear Magnetic Resonance (^{1}H NMR). Remarkably, the conversion of styrene oxide (SO) to styrene carbonate (SC) reached a yield of 99 % after 24 h of reaction. The calculated yield versus the aliphatic cyclohexene oxide is 71 %. Similar results were obtained by substituting the resin counter anion with Br$^-$, although the conversion kinetic was slower than the chloride. It is worth noticing that reactions took place in the mixture without adding the tetrabutylammonium bromide (TBAB), typically used as a co-catalyst to convert epoxides into carbonates. The recyclability of the as-prepared catalyst was evaluated for four reaction cycles, evidencing stable properties without significant depletion of CO$_2$ capture efficiency. Most importantly, the post-cleaning of the catalytic sponge is not required to be reused. Finally, the green chemistry metrics applied to the process demonstrated that our approach significantly mitigates risks and reduces environmental impact, thus elevating the overall cleanliness of our proof of concept.

Introduction

Carbon dioxide produced by anthropic activities is an undesired greenhouse gas whose effects worry the worldwide scientific community. To solve the problem, the inexpensive and abundant molecule can be converted into a new resource [1,2], producing chemical compounds greenly. In the last decade, cyclic carbonates can be obtained through the coupling reaction between CO$_2$

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and ring-strained heterocycles *via* milder reaction conditions if compared to the past [3]. A catalyst is needed since CO_2 is kinetically and thermodynamically stable to be converted without additional add. For polycarbonate plastic-based, CO_2 coupling with epoxide is a 100 % atom-economy reaction since all reactants are incorporated in the product. Furthermore, single five-membered cyclic carbonates are biodegradable liquids with low toxicity that can find further applications as aprotic polar solvents [4], electrolytes, degreasers, pesticides, and building blocks for biomedical materials such as drugs [3,5,6]. Several homogeneous and heterogeneous catalysts have been developed in the last years to be used in the catalytic fixation of CO_2 into epoxides to produce cyclic carbonates; both types of catalysts present pros and cons [7,8]. Compared to their homogeneous counterparts, heterogeneous catalytic systems are inevitably less active due to limited reactant migration versus the catalytic sites. However, the latter is considered more suitable for future industrial development and less impactful in terms of eco-sustainable use [9]. A comprehensive review reporting remarkable examples of heterogeneous catalysts that can work in mild conditions to produce cyclic carbonate was authored by M. North et al. [10]. As far as it is concerned, a challenge for such systems is to increase their catalytic activity to reach values comparable to homogeneous ones. One of the most used techniques to combine the high activity of homogeneous catalysts with simple and effective catalyst recovery is the "heterogenization" of active species by functionalized/immobilized support materials [11]. Essentially, a binary catalytic system gains the activation of CO_2 or epoxide molecules to trigger the coupling reaction [12]. This approach involves the design of catalysts, including Lewis acid sites, which activate the epoxide, and Lewis bases as nucleophilic species [13]. For this purpose, quaternary ammonium (or phosphonium) ionic liquids (ILs), and especially quaternary ammonium cations and halogen anions such as Cl^-, Br^-, and I^- [14–16] are among the most popular catalysts. The border between the two roles is difficult to establish [17]. Regarding the CO_2 coupling reaction with styrene oxide, Calò and coworkers demonstrated that TBAB alone is enough to catalyze the reaction at 120 °C and atmospheric pressure [18–21].

M. Razaghi reported, as a catalytic system, hollow mesoporous silica spheres impregnated with quaternary ammonium halides [22]. The success in a high-conversion rate of CO_2 under mild conditions was ascribed to the confinement effect of reactants inside the silica pores. Whatever the real contribution of alkyl ammonium salts, their addition as reaction solvent implies concerns from the environmental point of view. In addition, its presence in the mixture requires time and cost-consuming purification steps to yield the final product [23]. TBAB is also harmful to aquatic life with long-lasting effects, and it is suspected of damaging fertility [24].

This paper reports the synthesis and application of a new sustainable and reusable catalyst based on polymeric immobilized ammonium quaternary salt. Specifically, the most holistic and affordable approach was used to achieve our scope, selecting the monomer 2-(acryloyloxy)ethyl]trimethylammonium chloride ($AETMA^+Cl^-$). The latter contains the catalyst functionality and a polymerizable double bond. According to the notifications provided by companies to the European Chemical Agency in REACH registrations, no hazards have been classified for this monomer [25].

The corresponding polymer finds many applications in the water treatment industry, as well as in home and personal care. $AETMA^+Cl^-$ is a fossil raw-based product derived from the C3 value chain, which is not still replaceable with a biobased source. Nevertheless, it is synthesized with a quasi-quantitative yield using a catalyst that can be recycled for further processes [26].

A cryo-polymerization was selected to produce the heterogeneous catalyst, gaining a macroporous and shapable polymeric network suitable for reactant embedding. Undoubtedly, alkyl ammonium immobilization strategies have already been reported in the literature [27–29]; however, the resulting materials were derived from complicated synthetic pathways, costly reactants, or unsustainable processes. In our vision, as shown by Brzęczek-Szafran et al. [30] the less impacting strategy must be selected considering the catalyst scaling up. In light of this, our monolithic and macroporous materials can be proficiently used in a continuous catalytic bed and easily removed when exhausted. Looking forward to this vision, synthesis, conversion tests, and comparative measurements using TBAB were also performed and described herein. Furthermore, the CHEM21 Metrics Toolkit was applied to assess the sustainability of the chemicals and reactions of the proposed potential technology.

Experimental section
Chemical and reagents
The starting materials 2-(Acryloyloxy)ethyl]trimethylammonium chloride solution 80 %, *N,N'*-methylenebisacrylamide (MBAA), tetramethyl-ethylene-diamine (TEMED), ammonium persulfate (APS), styrene epoxide, cyclohexene epoxide, 1,2-epoxy-3-phenoxypropane, 4-vinyl-1-cyclohexene 1,2-epoxide, absolute ethanol (EtOH), deuterated chloroform ($CDCl_3$) were purchased from Sigma-Aldrich. A Milli-Q water purification system produced deionized water. ^1H NMR spectra were recorded using Bruker AvanceTM 400 MHz.

Synthesis of catalyst $AETMA^+Cl^-$
500 mg of AEMA (2.58 mmol) and 66 mg (0.4 mmol) of crosslinker agent *N,N'*-methylene bisacrylamide (MBAA) were put in a vial, and water was added. The mixture was stirred until complete dissolution and cooled. The amount of water was corrected to obtain a total content of polymerizable compounds of 10% w/v of the solution, then 1.5 % v/v of APS and TEMED at 10% w/v concentration was added. After stirring the mixture for 1 min, the solution was distributed into a 10 mL capped syringe and poured into a cryostatic bath at −15 °C for 24 h. Subsequently, the cryogel was thawed, washed with water and ethanol, and dried. The polymerization yield was 90 %.

Synthesis of catalyst $AETMA^+Br^-$
A monolithic piece of $AETMA^+Cl^-$ (210 mg) was immersed in a saturated solution of NaBr (10 mL) for 1 hour three times, then was washed four times with water and then with ethanol. The cryogel was finally dried under vacuum. The Cl/Br exchange yield was higher than 99 %.

Catalyst characterization

The catalyst AETMA was characterized by Fourier transform-infrared spectroscopy (FT-IR), and the spectra were recorded in absorbance mode (64 scans and 4 cm^{-1} resolution) in the 4000–400 cm^{-1} region using a Varian 640-IR by Agilent Technologies, with a ZnSe crystal fixed at the incident angle of 45 °.

The catalyst was subjected to thermogravimetric analyses (TGA) by using a thermogravimetric apparatus (TA Instruments Q500) under a nitrogen atmosphere (flow rate 60 mL/min) at 10 °C/min heating rate, from 40 °C to 800 °C. TGA sensitivity is 0.1 μg with a weighting precision of ± 0.01 %.

A Phenomenex microscope was used to study the synthesized material's morphology by scanning electron microscopy (SEM). Samples were pre-coated with gold sputter coating to increase conductivity before the test. Images were then captured to examine the cryogel morphology. The data were acquired and processed using Phenom Porometric 1.1.2.0 (Phenom-World BV, Eindhoven, The Netherlands). Energy-dispersive X-ray spectroscopy (EDX) was used to analyze the chemical elements material and determine its chemical composition.

General procedure for the synthesis of cyclic carbonates

Different epoxide (0.4 mmol) and catalysts (3 mg) were put in a 2 mL vial. 150 mg of CO_2 were added as dry ice. After a specific time and temperature, the reactor was cooled in an ice bath, and excess CO_2 was carefully vented off. The product was analyzed by ^{1}H NMR.

The time of frequency (TOF) of the catalyzed reactions was determined to achieve the conversion performance compared to other systems. TOF is the ratio between the mole of the reagent (n_r) and the product of time (in hours) with a mole of the active site of the catalyst by assuming that all the active sites have equal activity and the same possibility to be reached by the reagents.

$$TOF = \frac{n_r}{t \cdot n_{as}}$$

The Turnover Number (TON) measures the catalyst's maximum utilization potential. It represents the highest achievable yield from a catalytic center before its activity diminishes [31]. TON is calculated as the ratio between the moles of the reagent (n_r) and the moles of the active site within the catalyst.

$$TON = \frac{n_r}{n_{as}}$$

Reusability

To test the stability and recyclability of the synthesized catalyst, the reaction product was separated from the catalyst. The latter was reused without washing for further reactions between substituted epoxide and CO_2.

Results and discussion

It is well-recognized that alkali metal halides are among the most cheap, non-toxic, abundant, and easily recyclable catalysts due to the nucleophilicity of the halogen anions [32]. Quaternary ammonium cations with halogen anions are well-recognised to form cyclic carbonate compounds by CO_2 fixation with epoxydes. Starting from the fact that quaternary ammonium cations can (i) efficiently work in mild conditions to produce cyclic carbonates;

(ii) several successful examples of quaternary ammonium cations immobilized on silica, polymers, porphyrins were reported in the literature [3,33–37], our aim was the designing of an effective catalyst, simple to scale-up, without constraints in terms of numbers of synthetic pathways, use of unsustainable and toxic solvents, cost and time consumption.

Based on our expertise in cryogel production and material scale-up, we decided to test such a polymeric network, exploiting its ability to expose many active sites for the coupling reaction. Indeed, the idea was to combine the advantages of quaternary ammonium salts (e.g., catalytic activity, selectivity) and macroporous materials (e.g., large surface area, enhanced mass transfer). In this view, [2-(acryloyloxy)ethyl]trimethylammonium chloride (AETMA$^+$Cl$^-$) was chosen as a monomer for polymer synthesis thanks to its similarity to well-known co-catalyst used in the organic reaction of CO_2 conversion.

Synthesis and characterization of AETMA$^+$X$^-$

AETMA$^+$Cl$^-$ monomer underwent cryo-polymerization using MBAA as crosslinker and water as solvent (Fig. 1). This polymerization occurred at –15 °C, allowing the formation of ice crystals that, after thawing, left a macroporous structure [38,39]. In this case, the solvent acts as a porogen, allowing the realization of a porous material with sponge-like properties. The obtained cryogels can be fabricated in different shapes and sizes, including monoliths, rods, sheets, discs, spherical particles, etc. [40]. In catalysis, this can represent a significant advantage in industrial applications. Poly AETMA$^+$Br$^-$ was produced as described in the experimental section with a quasi-total substitution as confirmed by EDX analysis (Figure S2) to compare the efficiency of different halogenated salts.

FT-IR spectra confirmed the successful polymerization of the AETMA chloride since peaks in the 1000–800 cm^{-1} range related to the methylene (–C = C) group of the acrylic portion of the monomer disappearance owing to the polymerization (Fig. 2) [41].

The trimethylammonium chloride moiety ([N(CH$_3$)$_3$]$^+$Cl$^-$) exhibits characteristic peaks related to the quaternary ammonium salt. The N$^+$-CH$_3$ symmetric and asymmetric stretching vibrations are typically observed as sharp absorption bands around 2900–3000 cm^{-1} and 3100–3200 cm^{-1}, respectively. The chloride (Cl$^-$) ion may contribute to the absorption bands in the lower wavenumber region, around 500–600 cm^{-1}.

TGA measurements for halogenated polymeric salts were performed to prove the thermal stability of the catalysts at the temperature used for the CO_2 cycloaddition reaction. The thermal profiles are exhibited in Figure S1. The TG analyses showed that AETMA$^+$Cl$^-$ and AETMA$^+$Br$^-$ have excellent thermal stability up to 220 °C, with two steps of decomposition with the max decomposition rates at 267 and 426 °C for AETMA$^+$Cl$^-$ and 283 and 426 °C for AETMA$^+$Br$^-$, respectively. The two decomposition steps are reasonably caused by (i) the unzipping reaction of the acrylate part at a lower temperature and (ii) the ammonium salt decomposition [42]. The residue at 800 °C was found to be 8 % for AETMA$^+$Cl$^-$ and 18 % for AETMA$^+$Br$^-$, owing to the formation of gel-like structures. The greater amount of residue accounted for the AETMA$^+$Br$^-$ sample derived from the higher atomic weight bromine if compared to the chlorine species.
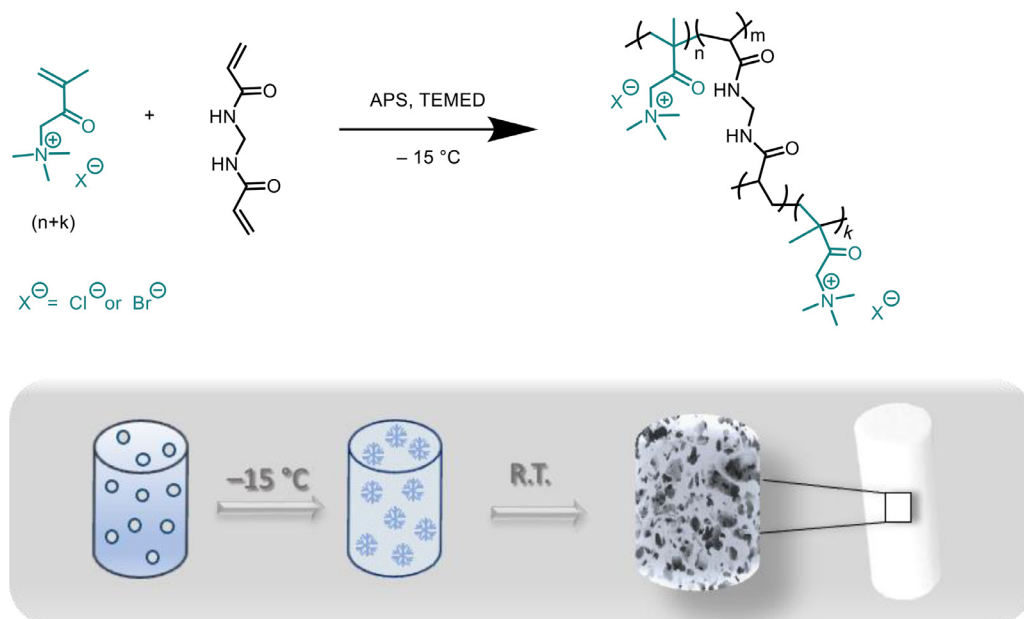
Fig. 1

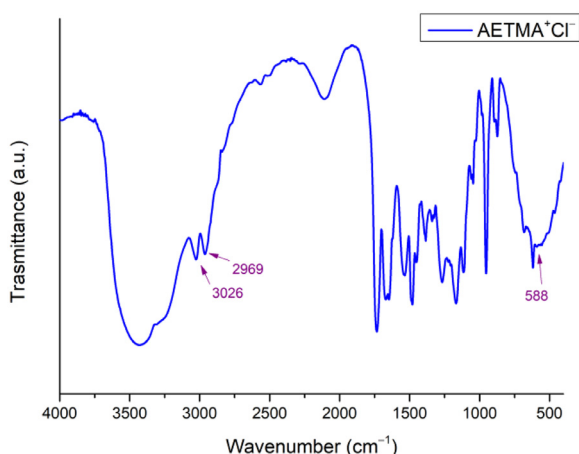Schematic representation of AETMA$^+X^-$ polymerization.

Fig. 2

FT-IR spectrum of AETMA$^+Cl^-$ polymer.

SEM analysis revealed a macroporous structure characteristic of cryogels for both samples, with a mean size pore distribution of 64.1 and 55.5 μm for AETMA$^+Cl^-$ and AETMA$^+Br^-$, respectively (Fig. 3).

To further investigate the cryogels' structure, the chemical composition of the AETMA$^+Cl^-$ and AETMA$^+Br^-$ was determined with EDX. As visible in Figure S2, the elements C, N, O, and Cl (or Br) presented a suitable range of chemical stoichiometry, corroborating the success of both syntheses.

Tuning the catalyst's performance

SO was used as a reference for a preliminary analysis to verify the formulated catalyst's efficiency. The coupling reactions were performed in neat styrene oxide (50 μL) at different temperatures (40, 80, 100, and 120 °C) with 150 mg of CO_2 and stopped after 24 h. As evidenced by ^{1}H NMR (Figure S3), the best conversion rate to styrene carbonate (SC) was obtained at 120 °C with a yield of 99 %. At 80 °C, the reaction was catalyzed, although only 15 % of the product was achieved.

The kinetic of the reaction was investigated employing both AETMA$^+Cl^-$ and AETMA$^+Br^-$ (Table 1) following carbonate formation by ^{1}H NMR (Figures 4 and S4, respectively). By using AETMA$^+Cl^-$, after 1 h of reaction, the peaks related to styrene epoxide protons at 2.81, 3.16, and 3.87 ppm are still visible, starting to disappear after 4 h. At that time, proton signals at 4.35, 4.82, and 5.69 ppm, indicating the formation of the styrene carbonate, appear in the ^{1}H NMR spectrum (Fig. 4).

As shown in Table 1, the rate of reaction was strictly related to the counterion, and this was in accordance with the reaction mechanism proposed below. In particular, the reaction resulted faster with AETMA$^+Cl^-$ with a rate of conversion that reached 91 % after 4 h, while the product yield was only 22 % by using AETMA$^+Br^-$ as the catalyst. Nevertheless, AETMA$^+Br^-$ gained a high conversion rate of up to 95 % at prolonged reaction time (8 h).

As stated in the literature, for both homo and heterogeneous systems, $Cl^- > Br^- > I^-$ is the order in which halogen anions perform the catalytic activity [36] This scale is consistent with the order of their nucleophilicity in an aprotic solvent [43], supporting the as-proposed reaction mechanism in Fig. 5. In this view, the crucial step is represented by the nucleophilic assault of halogen anions on epoxides, as confirmed by several esteemed works. It is worth noticing that in both cases, a period of induction is necessary to speed up the reaction rate.

This might be due to the formation of the product itself, which accelerates the reaction by acting as a solvent with chemical-physical characteristics different from epoxide. To compare
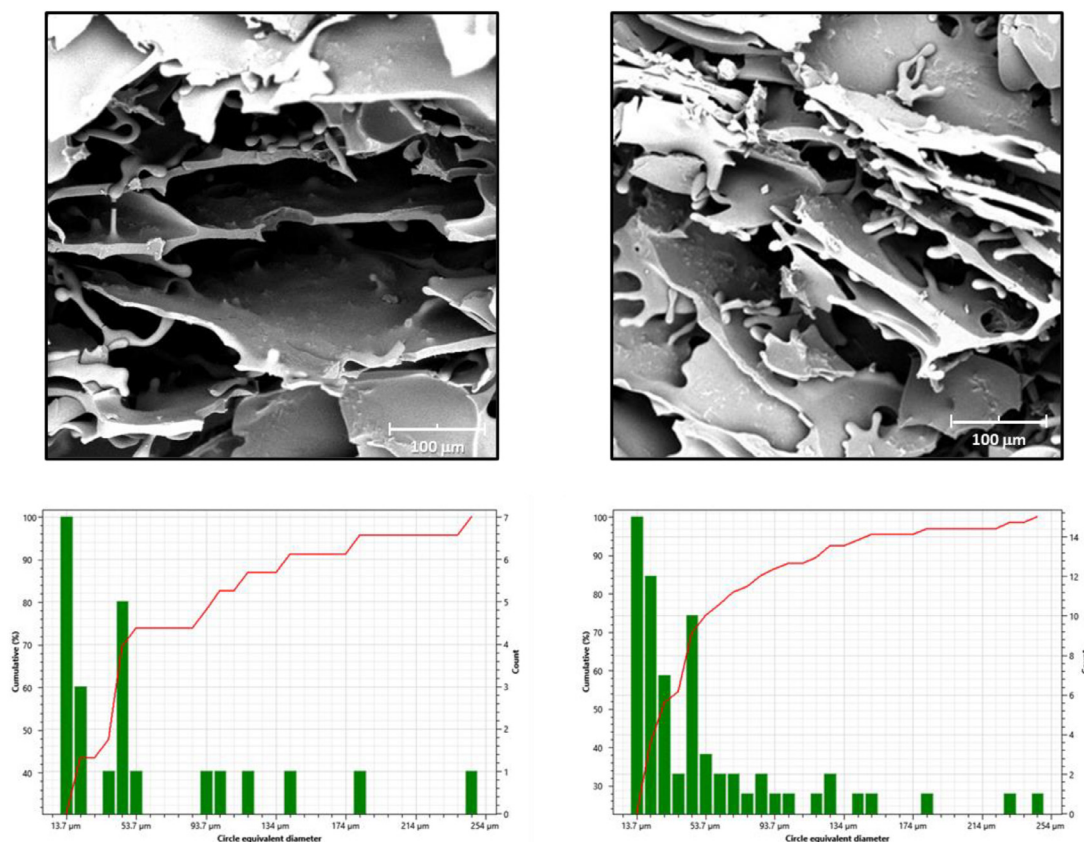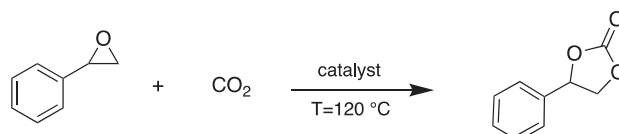
Fig. 3

SEM images of AETMA$^+$Cl$^-$ (left) and AETMA$^+$Br$^-$ (right) cryogels and relative pores distribution.

Table 1

Catalyst Screening for the Cycloaddition of Styrene Oxide with CO$_2$.

Time (h)	AETMA$^+$Cl$^-$		AETMA$^+$Br$^-$	
	Conversion (%)	TOF (h^{-1})	Conversion (%)	TOF (h^{-1})
1	5	1.6	0.5	0.2
4	91	7.2	22	2.1
8	98	3.9	95	4.5
24	99	1.3	99	1.5

the unsupported tetrabutylammonium halide catalysts with our material [44,45], TBAB was tested for the carboxylation of styrene oxide. The reaction was performed using a small amount of tetrabutylammonium bromide (0.1% mol compared to the total mol and 1% mol with respect to SO) at the same conditions as our synthesis. After 8 h, the calculated yield was around 80 %, confirming the data of Calò and coworkers [46]. Although this synthetic pathway could be viable, it cannot be considered approachable given an industrial scale-up minimizing waste and environmental impact.

The impact of varying CO$_2$ concentrations on the cycloaddition reaction was also assessed. As shown in Table 2, it is evident that there was a notable reduction in reaction rate after eight hours when employing 40 and 20 percent of the initial CO$_2$ amount.

TON calculation
A specific experiment was set up to determine the TON of AETMA$^+$Cl$^-$ catalyst. Precisely, 2 mg of catalyst was placed into a sealed, pressure-resistant glass reactor with a volume of 160 mL.
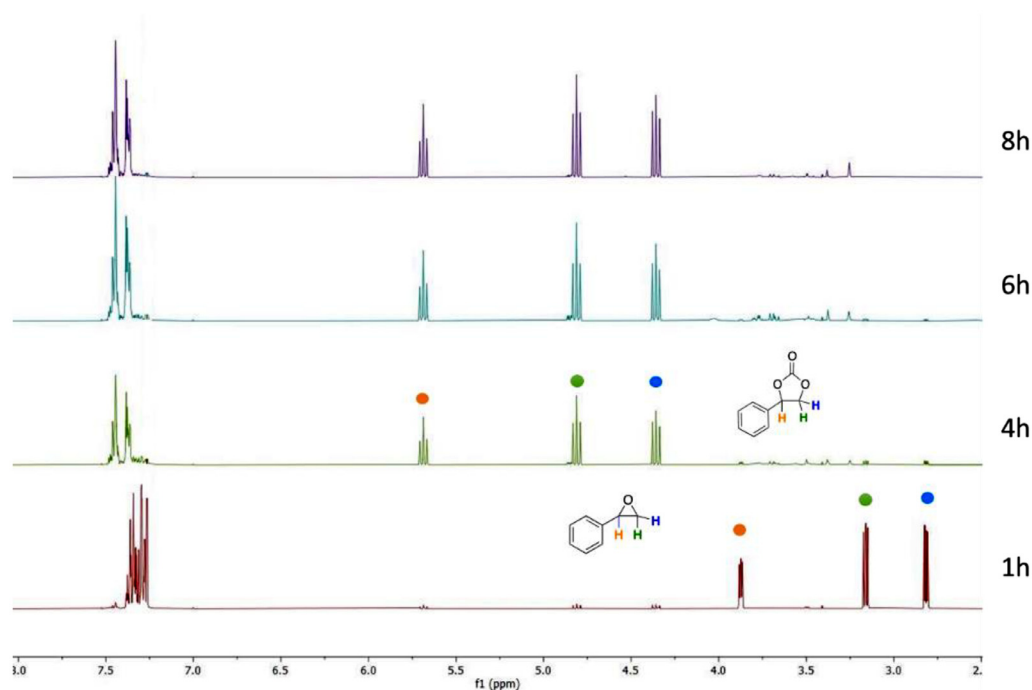
Fig. 4

Proton NMR spectra of CO_2 fixation into styrene oxide catalyzed by AETMA$^+$Cl$^-$ (120 °C), CDCl$_3$ as deuterium solvent, 400 MHz.
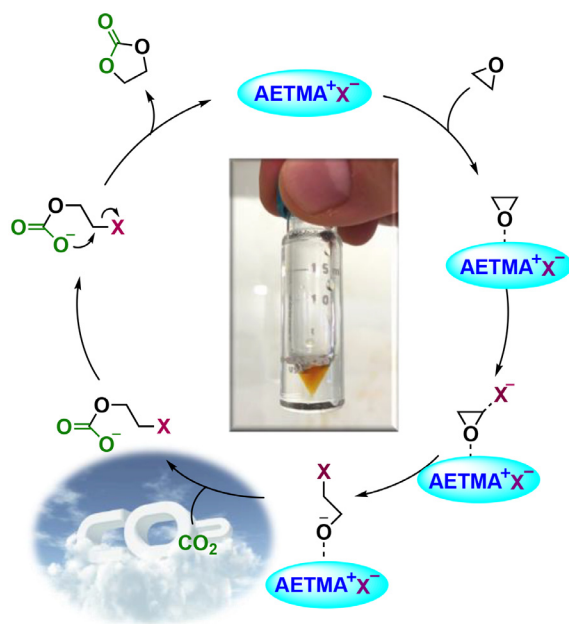

Fig. 5

Schematic proposal for cycloaddition of CO_2 and epoxides using AETMA$^+X^-$ catalysis.

Then, 3.6 mL of styrene epoxide and 10.5 g of solid CO_2 were added. The reactor was maintained at 120 °C, and the reaction proceeded for 10 days, resulting in an 80 % yield. An additional portion of CO_2 was added to the same reaction, proceeding for 24 h to assess any potential loss of catalytic activity. Ultimately, a reaction yield of 83 % was achieved. Under these conditions, the TON was greater than 3000.

Table 2

The conversion in carbonate as a function of CO_2 addition.

AETMA$^+$Cl$^-$

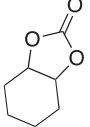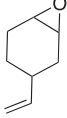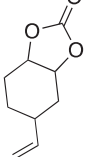| Time (h)	CO_2 utilized (mg)	Conversion
8	150	99 %
8	100	98 %
8	60	77 %
8	30	37 %
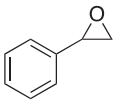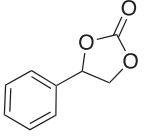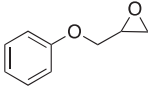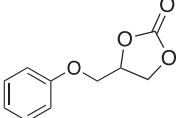
Substrate scope

To investigate the general applicability of AETMA$^+$Cl$^-$ with different substrates, several epoxides were selected for the cycloaddition reaction with CO_2 under the optimized reaction condition reported in Table 1. All epoxides were converted to the corresponding cyclic carbonates at 120 °C. Besides the SC conversion occurring with the highest yields, relevant results have been obtained using other substrates. In particular, 1,2-epoxy-3-phenoxypropane and cyclohexene oxide were converted into the correspondent carbonates with high conversions of 95 and 71 %, respectively (Table 3), whereas 4-vinyl cyclohexene oxide performed lower conversions.

The AETMA$^+X^-$ should operate through a proposed reaction mechanism shown in . Several studies have indicated that en bonding between the catalyst and substrate is critical in enhancing reactions [6]. Qu and coworkers [47] reported that hydrogen bonding at the solid/liquid interface can activate epoxides and stabilize ring-opening intermediates. Initially, the ammonium salt

Table 3

Synthesis of Carbonates from CO_2 and Various Epoxides Using $AETMA^+Cl^-$ as a Catalyst.

Entry	Epoxide	Epoxide (mg)	Carbonate	Carbonate (mg)	Yield (%)[a]
1		52.5		70.9	99
2		55.0		67.3	95
3		48.5		49.8	71
4		54.7		28.1	38

[a] Reaction conditions: epoxides (30 mmol), $AETMA^+Cl^-$ catalyst (3 mg). Temperature $T = 120$ °C. Yield and selectivity were measured by ^1H NMR.

of the catalyst interacts with the oxygen atom to activate the epoxide.

Subsequently, the halogen (bromine or chlorine) attacks the less hindered side of the epoxide, which is the rate-determining step, as suggested by the kinetic of the reaction, leading to the ring opening and the formation of an oxygen anion intermediate [6].

The intermediate can react with CO_2. Ring closure occurs, releasing cyclic carbonate and the catalyst sites accessible for a new cycle.

Catalyst recycling

The recyclability of $AETMA^+Cl^-$ was tested by recovering it from the reaction medium and taking out the reaction product. It is worth highlighting that the catalyst was recyclable for 4 cycles with no substantial loss in the catalytic activity, allowing the reduction of cost and the environmental impact; after 3 cycles of recycling, the yield of cyclic carbonate remained at 96 %, while it decreased to <90 % from the third run (Fig. 6). It is reasonable to suppose that the presence of reaction impurities causes the deactivation of part of the catalytic sites. This relevant aspect is under investigation. From preliminary results, the catalyst continued to be active for further tests, although with reduced activity.

Green chemistry metrics

The CHEM21 green metrics toolkit was applied to this study to assess the environmental impact of our procedure to synthesize cyclic carbonates [48]. This toolkit allows quantitative and qualitative evaluation of methodologies regarding their
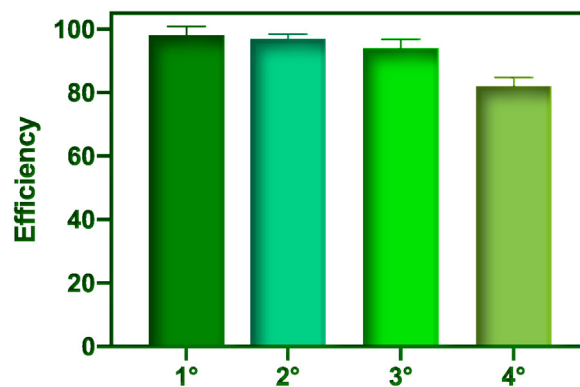

Fig. 6

Reusability of $AETMA^+Cl^-$ catalysis (efficiency vs. number of cycles).

sustainability and employs a multi-level evaluation process [49]. It begins with the Zero Pass, where initial screening considers health and safety risks associated with solvents and chemicals. The efficiency of the reaction in terms of conversion and yield was also considered. Promising routes can proceed beyond the First Pass, calculating the process mass intensity (PMI) to assess sustainability quantitatively [50]. PMI can be broken down into individual values for the reaction, solvents, and workup, helping identify areas for improvement. Once a procedure passes the First Pass, it undergoes Second and Third Pass evaluations, which are more suited for industrial-scale analysis and go beyond lab-scale research [51]. These evaluations include detailed energy analysis, cost assessment, renewable resource usage, and waste generation [52].

Table 4

Summary of the Results from the CHEM21 Green Metrics Toolkit Calculation.
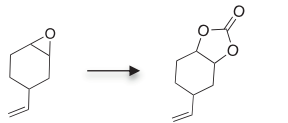
Epoxide/Carbonate	Catalyst	Temperature (°C)	Time (h)	Conversion (%)	Yield %	AE %	RME %	PMI g/g
styrene oxide → styrene carbonate	AE		8			100	32.8	3.1
	TM	120		99	99			
	A⁺Cl⁻							
phenyl glycidyl ether → carbonate	AE		8			97.6	30.4	3.3
	TM	120		95	95			
	A⁺Cl⁻							
cyclohexene oxide → carbonate	AE		8			100	25.0	4.1
	TM			71	71			
	A⁺Cl⁻							
vinylcyclohexene oxide → carbonate	AE		8			100	8.6	8.6
	TM	120		38	38			
	A⁺Cl⁻							
styrene oxide → styrene carbonate	TBAB	120	8	80	80	100	27.5	3.7

Table 5

List of catalysts and reaction parameters reported in the recent literature for the conversion of SO to SC.

Catalyst	Amount	Temperature (°C)	Pressure (atm)	Conversion (%)	Time (h)	TOF	Reference
TBAB/TBAI	50 g	120	1	83	4	1.3	[46]
Ionenes	4 mmol	120	1	90	8	—	[53]
Betaine hydroiodide	—	180	80	96		4.8	[54]
$Ph_3P^+Br^-$	5 wt.%	100	27	98	3	—	[55]
$PEG600-Ph_3P^+Br^-$							
Silica-supported ammonium and amino-pyridinium halides	0.9 mol	100	1	89	20	—	[56]
TEG/KI/MeOH	3.50	25	1	52	3	—	[57]
Ag^x/POM	100 mg	75	25	71	6	—	[58]
Amb-OH-I910	95 mg/0.21mmol	100	30	93	18	5.1	[59]
Salothen-t-Bu-Cr	0.05 mmol	80	11	100	23	—	[60]
LFe_2-O-NH_2/SiO_2	0.036 g	80	1	65	24	25	[61]

Analyzing the cycloaddition reactions of CO_2 with epoxides, it is evident that these reactions exhibit high selectivity, resulting in a reaction mass efficiency (RME) parameter comparable to the yield (Table 4). We also evaluated the process mass intensity (PMI) parameters by comparing total mass-based inputs to the mass of the generated product. Our findings indicate that the PMI values are notably low. As it turns out, our method is totally solvent-free, underscoring its environmentally friendly nature. Additionally, the catalyst itself can be deemed environmentally friendly since its production does not require the use of organic solvents or hazardous chemicals. When considering adherence to the principles of green chemistry, this catalyst receives green flags owing to catalyst activity, minimal loading, sustainable origin, low environmental impact, recyclability, and the eco-friendly nature of the workup procedure it entails.

Conclusions

Here, we proposed a new heterogeneous catalyst that converts CO_2 and epoxides into cyclic carbonates with yields up to 99 %. Our system showed remarkable performance compared to other catalysts reported in the literature (Table 5). Overall, quaternary ammonium salts are widely used as phase transfer catalysts in the fixation of CO_2 and other related reactions, enhancing reaction efficiency and enabling carbon dioxide utilization as a valuable feedstock. The material based on 2-[(acryloyloxy)ethyl]trimethylammonium chloride was synthesized by cryo-polymerization technique, obtaining a freestanding macroporous sponge with outstanding activity in producing aromatic and aliphatic carbonates. Water is used as a solvent to polymerize the catalyst, increasing the sustainability of the overall synthetic routes.

To date, the design of eco-sustainable processes and materials plays a key role in promoting low environmental impacts. In this view, our catalyst efficiently reduces the formation of unwanted by-products and waste and maintains its catalytic activity over multiple reaction cycles. In an optic of advancing sustainable chemistry and industrial practices, this implies an additional reduction of cost and, most importantly, waste generation. Finally, the as-prepared material, eliminating CO_2 and converting it into carbonate, performs the carbon capture and storage (CCS) well;

SC, obtained with yields of 99 %, finds great commercial interest (it can be used as a solvent for lithium batteries) since it is a non-toxic and a valuable precursor to produce polycarbonates. Additionally, our catalyst is recyclable and can be reused several times without further washing procedures. The analysis indicates that cryogel catalysts prioritize adherence to green chemistry principles and balancing factors such as catalyst activity, loading, origin, environmental impact, recyclability, and the workup procedure. Due to the growing awareness of environmental concerns and regulations, it is imperative to incorporate these considerations when designing innovative catalytic systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

CRediT authorship contribution statement

Sandro Dattilo: Data curation, Formal analysis, Writing – original draft. **Chiara Zagni:** Conceptualization, Supervision, Validation, Writing – original draft. **Tommaso Mecca:** Conceptualization, Investigation. **Vincenzo Patamia:** Methodology. **Giuseppe Floresta:** Methodology. **Pietro Nicotra:** Resources. **Sabrina C. Carroccio:** Supervision, Writing – review & editing. **Antonio Rescifina:** Supervision, Validation, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.giant.2024.100258.

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